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(54) Title: THERMALLY STABLE OIL-BASE DRILLING FLUID

(57) Abstract

An oil-base drilling fluid capable of being held at temperatures in excess of 400 °F while maintaining its yield point comprises (i) oil, (ii) a surfactant, (iii) an organophilic clay, (iv) a polymeric fluid loss control agent selected from the group consisting of polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene, natural rubber, butyl rubber, polymers consisting of at least two monomers selected from the group consisting of styrene, butadiene, isoprene, and vinyl carboxylic acid, and mixtures thereof, and (v) a sulfonated elastomer polymeric viscosifier.

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THERMALLY STABLE OIL-BASE DRILLING FLUID

BACKGROUND OF THE INVENTION

The present invention relates to oil-base drilling fluids and systems and processes for drilling a borehole in a subterranean formation.

Oil-base drilling muds and techniques for drilling boreholes in subterranean formations to recover hydrocarbons (e.g., oil and gas) are well known to those skilled in the art.

While tripping a drillstring, running logs, performing fishing operations, or conducting other procedures during a drilling operation, the drilling fluid or mud in the borehole remains stagnant and its temperature can reach, and remain at, the bottomhole temperature for several days.

SUMMARY OF THE INVENTION

According to one aspect of the invention, there is provided an oil-base drilling fluid comprising oil, a surfactant, a fluid loss control agent, and a viscosifier, characterized in that the fluid loss control agent is selected from the group consisting of polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene, natural rubber, butyl rubber, polymers consisting of at least two monomers selected from the group consisting of styrene, butadiene, isoprene, and vinyl carboxylic acid, and mixtures thereof and the viscosifier is a sulfonated elastomer polymer.

According to another aspect of the invention, there is provided an oil-base drilling fluid weighing about 7.5 to about 20 pounds per gallon and comprising: (a) about 25 to about 85 volume percent oil based on the total volume of the fluid; (b) about 1 to about 20 pounds per barrel (ppb) surfactant; (c) up to about 45 volume percent water based on the total volume of the fluid; (d) up to about 600 ppb weighting agent; (e) about 0.5 to about 30 ppb organophilic clay; (f) up to about 30 ppb auxiliary fluid loss control agent; (g) about 3 to about 12 ppb polymeric fluid loss

control agent selected from the group consisting of polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene, natural rubber, butyl rubber, polymers consisting of at least two monomers selected from the group consisting of styrene, butadiene, isoprene, and vinyl carboxylic acid, and mixtures thereof; (h) about 0.02 to about 2 weight percent sulfonated elastomer polymeric viscosifier; (i) up to about 60 ppb shale inhibiting salt; and (j) up to about 30 ppb lime.

According to a further aspect of the invention, there is provided a drilling system comprising: (a) at least one subterranean formation; (b) a borehole penetrating a portion of at least one of the subterranean formations; (c) a drill bit suspended in the borehole; and (d) a drilling fluid located in the borehole and proximate the drill bit, wherein the drilling fluid is the oil-base drilling fluid, as described above.

According to a still further aspect of the invention, there is provided a method for drilling a borehole in a subterranean formation, the method comprising the steps of: (a) rotating a drill bit at the bottom of the borehole and (b) introducing a drilling fluid into the borehole (i) to pick up drill cuttings and (ii) to carry at least a portion of the drilling cuttings out of the borehole, wherein the drilling fluid is the oil-base drilling fluid, as described above.

Organophilic clays used in oil-base drilling fluids have been observed to degrade when the drilling fluid is maintained at bottomhole temperatures exceeding 400° F. This degradation lowers the yield point of the drilling fluid--rendering the drilling fluid incapable of suspending solids and resulting in expensive drilling problems such as weighting agent sagging, mud density variations, solids settling, stuck drillpipe, poor hole cleaning, excessive fluid loss to the formation, and poor cement jobs.

The present invention provides an oil-base drilling fluid capable of being held at temperatures in excess of 400° F while maintaining its yield point. The oil-base fluid comprises (i) oil, (ii) a surfactant, (iii) an organophilic

clay, (iv) a polymeric fluid loss control agent selected from the group consisting of polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene, natural rubber, butyl rubber, polymers consisting of at least two monomers selected from the group consisting of styrene, butadiene, isoprene, and vinyl carboxylic acid, and mixtures thereof, and (v) a sulfonated elastomer polymeric viscosifier.

In addition, a drilling system and a method for drilling a borehole are also provided by the invention. The drilling system comprises (a) at least one subterranean formation, (b) a borehole penetrating a portion of at least one of the subterranean formations, (c) a drill bit suspended in the borehole, and (d) the above drilling fluid located in the borehole and proximate the drill bit.

Regarding the method for drilling a borehole of the present invention, this method comprises the steps of (a) rotating a drill bit at the bottom of the borehole and (b) introducing the aforesaid drilling fluid into the borehole (i) to pick up drill cuttings and (ii) to carry at least a portion of the drill cuttings out of the borehole.

DESCRIPTION OF THE DRAWINGS

The improved heat aged performance characteristics and other features, aspects, and advantages of the present invention will become better understood with reference to the following description, appended claims, and accompanying drawings where:

Figure 1 is a graph depicting the plastic viscosity as a function of aging time at about 400° F of three commercially available drilling fluids alleged by their suppliers to possess good thermal stability.

Figure 2 is a graph depicting the yield point as a function of aging time at about 400° F of the three commercially available drilling fluids shown in Figure 1.

Figure 3 is a graph depicting the high temperature-high pressure fluid (HTHP) loss as a function of aging time at about 400° F of the three commercially available drilling fluids shown in Figure 1.

Figure 4 is a graph depicting the top oil separation as a function of aging time at about 400° F of the three commercially available drilling fluids shown in Figure 1.

Figure 5 is a graph depicting the plastic viscosity as a function of aging time at about 400° F of an exemplary drilling fluid of the present invention and another two commercially available drilling fluids alleged by their suppliers to possess better thermal stability than the drilling fluids depicted in Figures 1-4.

Figure 6 is a graph depicting the yield point as a function of aging time at about 400° F of the exemplary drilling fluid of the present invention and the other two commercially available drilling fluids shown in Figure 5.

Figure 7 is a graph depicting the HTHP loss as a function of aging time at about 400° F of the exemplary drilling fluid of the present invention and the other two commercially available drilling fluids shown in Figure 5.

Figure 8 is a graph depicting the top oil separation as a function of aging time at about 400° F of the exemplary drilling fluid of the present invention and the other two commercially available drilling fluids shown in Figure 5.

DETAILED DESCRIPTION OF THE INVENTION

Without being bound by the theory of its operation, it is believed that the oil-based drilling fluid of the present invention maintains it yield point upon aging at temperatures greater than about 400° F by, among other things, the unique combination of three ingredients, namely, a thermally stable organophilic clay, a polymeric fluid loss control agent, and a sulfonated elastomeric polymeric viscosifier. Exemplary thermally stable organophilic clays include, but are not necessarily limited to, hectorite and bentonite, with hectorite being the more preferred. The organophilic clays can be employed either individually or in combination.

Illustrative polymeric fluid loss control agents include, but are not limited to, polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene,

natural rubber, butyl rubber, polymers consisting of at least two monomers selected from the group consisting of styrene, butadiene, isoprene, and vinyl carboxylic acid. Individual or mixtures of polymeric fluid loss control agents can be used in the oil base drilling fluid of this invention. Exemplary polymeric fluid loss control agents are described in SPE 13560 (1985), this article being incorporated herein in its entirety by reference.

The preferred polymeric fluid loss control agents are styrene-butadiene copolymers. Characteristics of exemplary styrene-butadiene copolymers are listed in the following Table I:

TABLE I

	Union Oil Company of California Product Number			
Characteristic	76RES4176	76RES4105	76RES4106	76RES4470
Styrene/-Butadiene Ratio	50/50	57/43	90/10	67/33
Surfactant Type	Anionic	Anionic	Anionic	Anionic
Tg, °C	-22	-11	76	12
pH	9.0	6.0	6.5	9.0

All the styrene/butadiene copolymers described in above Table I also contain about 1 to about 3 weight percent copolymerized carboxylic acid (e.g., itaconic acid and acrylic acid).

The sulfonated elastomer polymeric viscosifier is preferably a neutralized sulfonated elastomer polymer having about 5 to about 100 milliequivalents of sulfonate groups per 100 grams of sulfonated polymer. More preferably, the neutralized sulfonated elastomer polymer has about 5 to about 50 milliequivalents, and most preferably about 5 to about 30 milliequivalents, of sulfonate groups per 100 grams of sulfonated polymer.

Preferably, the sulfonated elastomer polymeric viscosifier is derived from an elastomer polymer selected from the group consisting of ethylene-propylene-diene monomer

(EPDM) terpolymers, copolymers of isoprene and styrene sulfonate salt, copolymers of chloroprene and styrene sulfonate salt, copolymers of isoprene and butadiene, copolymers of styrene and styrene sulfonate salt, copolymers of butadiene and styrene sulfonate salt, copolymers of butadiene and styrene, terpolymers of isoprene, styrene, and styrene sulfonate salt, terpolymers of butadiene, styrene, and styrene sulfonate salt, butyl rubber, partially hydrogenated polyisoprenes, partially hydrogenated polybutylene, partially hydrogenated natural rubber, partially hydrogenated buna rubber, partially hydrogenated polybutadienes, and Neoprene. Methods for obtaining and characteristics of sulfonated elastomer polymers are known to those skilled in the art. See, for example, U.S. Patent 4,447,338, U.S. Patent 4,425,462, U.S. Patent 4,153,588, U.S. Patent 4,007,149, U.S. Patent 3,912,683, and U.K. Patent Application 2,212,192, these documents being incorporated in their entirety by reference.

Typically, the oil-base drilling fluid of the present invention contains the ingredients and properties set forth in the following Table II:

TABLE II

Ingredient	Typical	More Typical
Oil, volume %[a]	25-85	50-60
Surfactant (active), pounds per barrel (ppb)[b,g]	1-20	1-10
Water, volume %[a]	up to 45	10-20
Weighting agent, ppb	up to 600	150-400
Organophilic clay, ppb	0.5-30	1-10
Auxiliary fluid loss control agent, ppb	up to 30	2-15
Polymeric fluid loss control agent, ppb[c]	3-12	5-10
Sulfonated elastomer polymeric viscosifier, ppb[d]	0.02-2	0.05-1.5
Shale inhibiting salt, ppb	up to 60	20-30
Lime, ppb[e]	up to 30	1-10
Property		
Density, ppg[f]	7.5-20	9-16

a. Volume percent is based on the total volume of the drilling fluid.

b. As used in the specification and claims, the term "surfactant" means a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). As used in the foregoing definition of surfactant, the term "interface" indicates a boundary between any two immiscible phases and the term "surface" denotes an interface where one phase is a gas, usually air. Exemplary ingredients referred to as surfactants by those skilled in the art include emulsifiers and oil wetting agents.

c. The polymeric fluid loss control agent is preferably present in the drilling fluid in a concentration of about 6 to about 9 ppb.

d. The sulfonated elastomer polymeric viscosifier is preferably present in the drilling fluid in a concentration of about 0.1 to about 1 ppb.

e. As used in the specification and claims, the term "lime" means quicklime (CaO), quicklime precursors, and hydrated quicklime (e.g., slaked lime ($Ca(OH)_2$)).

f. ppg denotes pounds per gallon.

g. The parts per barrel (ppb) is based upon the final composition of the drilling fluid.

The volumetric ratio of oil to water in the drilling fluid of the present invention ranges from about 100:0 to about 50:50.

Preferably, the weight ratio of the polymeric fluid loss control agent to the sulfonated elastomer polymeric viscosifier is about 1.5:1 to about 50:1, more preferably about 3:1 to about 20:1, and most preferably about 5:1 to about 10:1.

Oils, surfactants, weighting agents, and shale inhibiting salts typically used in oil-base drilling fluids are suitable for use in the present invention. For example, exemplary oils, surfactants, and weighting agents are described in U.S. Patent 4,447,338 and U.S. Patent 4,425,462, these patents having previously been incorporated herein in their entireties by reference.

Typical shale inhibiting salts are alkali metal and alkaline-earth metal salts. Calcium chloride and sodium chloride are the preferred shale inhibiting salts.

As used in the specification and claims, the term "auxiliary fluid loss control agents" means particles (other than the polymeric fluid loss control agent discussed above) having a size only slightly smaller than that of the pore openings in the formation. The auxiliary fluid loss control agent is used to form a filter cake on the surface of a wellbore to reduce the loss of drilling fluid solids and liquids to the formation. Exemplary auxiliary fluid loss control agents include, but are not limited to, sulfonated asphaltenes, asphaltenes, lignite, and gilsonite. The

softening point of the auxiliary fluid loss control agent is as high as possible, preferably at least about 300° F, and more preferably at least about 350° F. Due to its high softening point, gilsonite is the most preferred auxiliary fluid loss control agent. Commercially available gilsonite has a softening point within the range of about 290° to about 400° F.

The drilling fluid is preferably prepared by mixing the constituent ingredients in the following order: (a) oil, (b) organophilic clay, (c) surfactant, (d) lime, (e) an aqueous solution comprising water and the shale inhibiting salt, (f) auxiliary fluid loss control agent, (g) weighting agent, (h) polymeric fluid loss control agent, and (i) sulfonated elastomer polymeric viscosifier.

The preferred plastic viscosity, yield point, high temperature-high pressure (HTHP) fluid loss, and top oil separation ranges for the drilling mud of the present invention are set forth in the following Table III.

TABLE III

	Preferred Range
Plastic Viscosity, cp	about 25 to about 48
Yield Point, lb/100sqft	about 10 to about 32
HTHP Fluid Loss, ml	about 1 to about 23
Top Oil Separation, ml	less than about 25

EXAMPLES

The following examples (which are intended to illustrate and not limit the invention, the invention being defined by the claims) compare various properties of an exemplary drilling fluid within the scope of the present invention (Example 1) with commercially available drilling fluids (Comparative Examples 2-7). In addition, Examples 8-11 demonstrate that different styrene/butadiene copolymers are suitable for use in the drilling fluids of this invention. The effect of varying sulfonated elastomer polymeric viscosifier and polymeric fluid loss control agent

concentrations on the properties of drilling fluids is shown in Examples 12-18.

EXAMPLE 1

An exemplary oil-base drilling fluid or mud (about 5 lab barrels, each lab barrel containing about 350 ml) within the scope of the present invention was formulated as shown in the following Table IV. The ingredients were sequentially added in the order set forth in Table IV. After the addition of each ingredient, the resulting composition was mixed for the indicated mixing time prior to adding a subsequent ingredient to the composition.

TABLE IV

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	205 ml (0.586 bbl)	N/A[a]
Inventone 38H brand amine-treated hectorite	3 ppb	30[b]
Versamul I brand primary emulsifier	4 ppb)	
Versacoat I brand	)	
oil wetting agent	5 ppb)-->	10
Versawet I brand surfactant	3 ppb)	
Lime ($Ca(OH)_2$)	10 ppb	10
Brine solution	30	
Water	51.5 ml (0.147 bbl)	
$CaCl_2$	26.3 ppb	
Versatrol brand gilsonite	10 ppb	15
Barite	269 ppb	20
HT brand polymeric fluid loss control agent	6 ppb	10
Tek Mud 1949 brand sulfonated elastomer polymeric viscosifier	1 ppb	35

a. N/A denoted not applicable.

b. The amine-treated hectorite was slowly added to the oil.

One sample was used to check the initial rheological properties. Samples to be aged were tested in duplicate, i.e., two samples were aged for about 24 hours and another two samples were aged for about 72 hours. The age-tested samples were placed into aging bombs in the presence of about 100 psi nitrogen and rolled at about 400° F. After aging, the amount of top oil separation was measured and the consistency of the drilling fluid noted. The age-tested samples were then remixed and their rheological properties checked. Both the initial and age-tested rheological properties were measured at about 150° F. The results are set forth below in Table V, with the plastic viscosity (PV), yield point (YP), high temperature-high pressure (HTHP) fluid loss, and top oil separation being plotted in Figures 5-8, respectively.

TABLE V

		After Hot Rolling At 400° F	
	Initial	24 Hours	72 Hours
Mud Weight, ppg	12.9		
E.S., volts[a]	620	283	322
Dial reading[b],			
600 rpm	110	102	95
300 "	70	63	56
200 "	56	49	42
100 "	38	32	28
6 "	21	11	7.5
3 "	20	10	6.5
Gel Strength[c],			
10 sec/10 min	20/33	10/18	6/13
PV, cp[d]	40	40	39
YP, lbs/100sqft[e]	30	23	17
HTHP fluid loss, ml[f]	1.4	4	4
Top oil separation, ml[g]		16	18

a. E.S. denotes electrical stability and was measured according to the procedure described in Recommended Practice - Standard Procedure for Field Testing

Drilling Fluids, Recommended Practice 13B (RP 13B), Twelfth Edition, September 1, 1988, American Petroleum Institute, Washington, DC (hereinafter referred to as "API"), page 28.

b. Dial readings were obtained using a 115-volt motor driven viscometer described in API, pages 7-9, sections 2.4 to 2.5.

c. Gel strength for 10 seconds and 10 minutes was determined in accordance with the procedure discussed in API, page 9, section 2.5, paragraphs f and g, respectively.

d. PV was determined in accordance with the procedure and calculations discussed in API, page 9, sections 2.5 to 2.6.

e. YP was determined in accordance with the procedure and calculations discussed in API, page 9, sections 2.5 to 2.6.

f. HTHP was determined in accordance with the procedure discussed in API, page 12, section 3.5.

g. Top oil separation was determined by decanting and measuring the oil layer above the solids in the age-tested drilling fluid present in aging bomb.

COMPARATIVE EXAMPLES 2-7

In comparative Examples 2-7, six different high temperature service company drilling fluids (about 5 lab barrels each) were prepared using recipes and mixing procedures supplied by the service companies. One sample of each of the different drilling fluids was used to check the initial rheological properties. Each aged sample was tested in duplicate, i.e., two samples of each different drilling fluid were aged for about 24 hours and another two samples were aged for about 72 hours. The age-tested samples were placed into aging bombs in the presence of about 100 psi nitrogen and rolled at about 400° F. After aging, the amount of top oil separation was measured and the consistency of the drilling fluid noted. The age-tested samples were then remixed and their rheological properties checked. Both the

initial and age-tested rheological properties were measured at about 150° F. The results are set forth below in Tables VI to XI, with the PV, YP, HTHP fluid loss, and top oil separation data for Examples 2-4 being respectively plotted in Figures 1-4 and the PV, YP, HTHP fluid loss, and top oil separation data for Examples 5-7 being plotted in Figures 5-8, respectively.

TABLE VI

MILPARK INVERT EMULSION DRILLING FLUID #1

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	0.61 bbl	N/A[a]
Carbo-Tec brand high temperature emulsifier	7 ppb)	
Carbo-Mul brand	)--->	3
emulsifier and wetting agent	8 ppb)	
Quick lime	5 ppb	3
Brine solution	10	
Water	0.153 bbl	
$CaCl_2$	29.4 ppb	
Carbo-Gel brand hectorite-based organophilic clay	3.5 ppb	3
Tek Mud 1949 brand sulfonated elastomer polymeric viscosifier	0.1 ppb	3
Carbo Trol HT brand polymeric fluid loss control agent	9 ppb	3
Barite	240 ppb	10

a. N/A denoted not applicable.

MILPARK INVERT EMULSION DRILLING FLUID #1

		After Hot Rolling At 400° F	
	Initial	24 Hours	72 Hours
Mud Weight, ppg	12.0		
E.S., volts[a]	422	457	567
Dial reading[b],			
600 rpm	45	85	98
300 "	25	49	53
200 "	17	36	38
100 "	10	23	23
6 "	3	3	3
3 "	2	2	2

Gel Strength[c],

TABLE VI (continued)

10 sec/10 min	10/2	2/5	4/2
PV, cp[d]	20	36	44.5
YP, lbs/100sqft[e]	5	13	8.5
HTHP fluid loss, ml[f]	4.4	25.5	110
Top oil separation, ml[g]		7	55

a-g. See Table V, footnotes.

TABLE VII

MILPARK INVERT EMULSION DRILLING FLUID #2

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	0.61 bbl	N/A[a]
Carbo-Tec brand high temperature emulsifier	7 ppb)	
	)--->	3
Carbo-Mul brand emulsifier and wetting agent	8 ppb)	
Quick lime	5 ppb	10
Brine solution	3	
Water	0.153 bbl	
$CaCl_2$	29.4 ppb	
Carbo-Gel brand hectorite-based organophilic clay	2 ppb	3
Tek Mud 1949 brand sulfonated elastomer polymeric viscosifier	0.75 ppb	3
PE-0140 brand latex polymer	2 ppb	3
Carbo Trol HT brand polymeric fluid loss control agent	10 ppb	3
Barite	240 ppb	10

a. N/A denoted not applicable.

TABLE VII (continued)

MILPARK INVERT EMULSION DRILLING FLUID #2

	Initial	After Hot Rolling At 400° F 24 Hours	After Hot Rolling At 400° F 72 Hours
Mud Weight, ppg	12.1		
E.S., volts[a]	375	511	465
Dial reading[b],			
600 rpm	50	132	119
300 "	28	84	70
200 "	20	68	54
100 "	13	47	35
6 "	4	21	12
3 "	3	19	11
Gel Strength[c], 10 sec/10 min	3/10	19/35	10/23
PV, cp[d]	22	48	48.5
YP, lbs/100sqft[e]	6	36	21.5
HTHP fluid loss, ml[f]	2.6	12.0	13.0
Top oil separation, ml[g]		30	68[h]

a.-g. See Table V, footnotes.

h. Drilling mud was severely caked in the bottom of the aging bomb.

TABLE VIII

M-I INVERT EMULSION DRILLING FLUID

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	0.586 bbl	N/A[a]
VG-69 brand hectorite-based organophilic clay	6 ppb	30
Versamul I brand primary emulsifier	4 ppb)	
Versacoat I brand	)	

TABLE VIII (continued)

oil wetting agent	5 ppb)--->	10
Versawet I brand surfactant	3 ppb)	
Lime ($Ca(OH)_2$)	10 ppb	10
Brine solution	30	
Water	51.5 ml (0.147 bbl)	
$CaCl_2$	26.3 ppb	
Versatrol brand gilsonite	10 ppb	15
HT brand polymeric fluid loss control agent	6 ppb	30
Barite	269 ppb	20

a. N/A denoted not applicable.

M-I INVERT EMULSION DRILLING FLUID

		After Hot Rolling At 400° F	
	Initial	24 Hours	72 Hours
Mud Weight, ppg	12.8		
E.S., volts[a]	343	283	296
Dial reading[b],			
600 rpm	67	59	62
300 "	41	29	30
200 "	32	19	20
100 "	21	10	10
6 "	7	1	1
3 "	6	1	1
Gel Strength[c], 10 sec/10 min	10/6	1/1	1/1
PV, cp[d]	26	30	32
YP, lbs/100sqft[e]	15	-1	-2
HTHP fluid loss, ml[f]	18	3	2
Top oil separation, ml[g]		32	40

a.-g. See Table V, footnotes.

TABLE IX

BARIOD INVERT EMULSION DRILLING FLUID #1

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	0.58 bbl	N/A[a]
Invermul NT brand oil mud emulsifier	4 ppb	2
EZmul NT brand oil mud emulsifier	10 ppb	2
Duratone HT brand amine treated lignite fluid loss control agent	13 ppb	2
Lime	8 ppb	5
Bentone 38 brand hectorite-based organophilic clay	8 ppb	2
Brine solution	10	
Water	0.13 bbl	
$CaCl_2$	37.4 ppb	
RM-63 brand polymeric fatty acid	1 ppb	2
Barite	269 ppb	35

a. N/A denoted not applicable.

TABLE IX (continued)

BARIOD INVERT EMULSION DRILLING FLUID #1

	Initial	After Hot Rolling At 400° F	
		24 Hours	72 Hours
Mud Weight, ppg	13.8		
E.S., volts[a]	2000	327	258
Dial reading[b],			
600 rpm	160	105	126
300 "	136	62	76
200 "	118	47	57
100 "	95	29	34
6 "	57	5	4
3 "	54	4	3
Gel Strength[c], 10 sec/10 min	75/54	4/24	17/3
PV, cp[d]	24	43	50
YP, lbs/100sqft[e]	112	19	25.5
HTHP fluid loss, ml[f]	2.4	3.4	8
Top oil separation, ml[g]		16	0

a.-g. See Table V, footnotes.

TABLE X

BARIOD INVERT EMULSION DRILLING FLUID #2

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	0.58 bbl	N/A[a]
Invermul NT brand oil mud emulsifier	4 ppb	2
EZmul NT brand oil mud emulsifier	10 ppb	2
Duratone HT brand amine treated lignite fluid loss control agent	13 ppb	2
Lime	8 ppb	5
Geltone IV brand organophilic clay-polymer blend	8 ppb	2
Brine solution		10
Water	0.13 bbl	
$CaCl_2$	37.4 ppb	
RM-63 brand polymeric fatty acid	1 ppb	2
Barite	263 ppb	35

a. N/A denoted not applicable.

TABLE X (continued)

BARIOD INVERT EMULSION DRILLING FLUID #2

	Initial	After Hot Rolling At 400° F 24 Hours	After Hot Rolling At 400° F 72 Hours
Mud Weight, ppg	13.0		
E.S., volts[a]	726	208	276
Dial reading[b],			
600 rpm	80	54	54
300 "	50	27	27
200 "	40	19	18
100 "	39	11	10
6 "	14	1	2
3 "	13	1	1
Gel Strength[c], 10 sec/10 min	13/30	1/2	1/4
PV, cp[d]	30	27	26.5
YP, lbs/100sqft[e]	20	0	1
HTHP fluid loss, ml[f]	2.6	4.6	8.6
Top oil separation, ml[g]		0	0

a.-g. See Table V, footnotes.

TABLE XI

IDF INVERT EMULSION DRILLING FLUID

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	0.55 bbl	N/A[a]
Interdrill Emul brand oil mud emulsifier	3 ppb	5
Interdrill Fl brand fluid loss reducer and secondary emulsifier	7 ppb	2
Interdrill OW brand oil wetting agent	1 ppb	2
Interdrill ESX brand high temperature emulsion/-contamination stabilizer	5 ppb	2
Lime	12 ppb	5
Vistone HT brand organophilic clay	8 ppb	2
Brine solution		10
Water	0.147 bbl	
$CaCl_2$	21.7 ppb	
Trudrill S brand asphaltene fluid loss control agent	9 ppb	2
Barite	266 ppb	20

a. N/A denoted not applicable.

TABLE XI (continued)

IDF INVERT EMULSION DRILLING FLUID

	Initial	After Hot Rolling At 400° F 24 Hours	72 Hours
Mud Weight, ppg	13.0		
E.S., volts[a]	133	557	870
Dial reading[b],			
600 rpm	108	63	72
300 "	72	32	38
200 "	61	22	28
100 "	45	12	17
6 "	23	1	3
3 "	21	1	2
Gel Strength[c], 10 sec/10 min	42/21	1/2	18/2
PV, cp[d]	36	31	33.5
YP, lbs/100sqft[e]	36	1	4.5
HTHP fluid loss, ml[f]	1.0	3.0	3.1
Top oil separation, ml[g]		0	0

a.-g. See Table V, footnotes.

A comparison of the results depicted in Figures 1-8 graphically indicates that the only drilling mud possessing satisfactory initial and aged plastic viscosity, yield point, HTHP fluid loss loss, and top oil separation characteristics is the exemplary drilling fluid within the scope of the present invention.

EXAMPLES 8-11

EXEMPLARY DRILLING FLUIDS CONTAINING DIFFERENT STYRENE/BUTADIENE POLYMERS

Using the different styrene/butadiene polymers set forth above in Table I, exemplary oil-base drilling fluids (about 5 lab barrels each) within the scope of the present invention were formulated as shown in the following Table XII:

TABLE XII

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	205 ml (0.586 bbl)	N/A[a]
Inventone 38H brand amine-treated hectorite	3 ppb	30[b]
Versamul I brand primary emulsifier	4 ppb	
Versacoat I brand oil wetting agent	5 ppb	10
Versawet I brand surfactant	3 ppb	
Lime ($Ca(OH)_2$)	10 ppb	10
Brine solution		30
Water	51.5 ml (0.147 bbl)	
$CaCl_2$	26.3 ppb	
Versatrol brand gilsonite	10 ppb	15
Barite	269 ppb	20
Styrene/Butadiene polymer	6 ppb	10
Tek Mud 1949 brand sulfonated elastomer polymeric viscosifier	1 ppb	35

a. N/A denoted not applicable.

b. The amine-treated hectorite was slowly added to the oil.

One sample of each drilling fluid was used to check the initial rheological properties. Samples to be aged for about 72 hours were tested in duplicate, while only one sample was used for those to be age-tested for about 24 hours. The age-tested samples were placed into 8 aging bombs in the

presence of about 100 psi nitrogen and rolled at about 400° F. After aging, the amount of top oil separation was measured and the consistency of the drilling fluid noted. The age-tested samples were then remixed and their rheological properties checked. Both the initial and age-tested rheological properties were measured at about 150° F. The results are set forth below in Table XIII.

TABLE XIII

A. 76RES4176

	Initial	After Hot Rolling At 400° F 24 Hours	After Hot Rolling At 400° F 72 Hours
E.S., volts[a]	794	338	300
Dial reading[b],			
600 rpm	110	132	126
300 "	70	82	72
200 "	56	66	54
100 "	39	44	34
6 "	22	14	8
3 "	21	13	6
Gel Strength[c], 10 sec/10 min	21/32	12/22	6/12
PV, cp[d]	40	50	54
YP, lbs/100sqft[e]	30	32	18
HTHP fluid loss, ml[f]	6	18	11
Top oil separation, ml[g]		25	24

TABLE XIII (continued)

B. 76RES4105

	Initial	After Hot Rolling At 400° F 24 Hours	After Hot Rolling At 400° F 72 Hours
E.S., volts[a]	654	414	341
Dial reading[b],			
600 rpm	105	94	109
300 "	69	59	67
200 "	56	47	53
100 "	39	33	35
6 "	25	14	13
3 "	24	13	11
Gel Strength[c], 10 sec/10 min	24/28	13/25	11/19
PV, cp[d]	36	35	43
YP, lbs/100sqft[e]	33	24	24
HTHP fluid loss, ml[f]	3.2	20	12
Top oil separation, ml[g]		28	27

TABLE XIII (continued)

C. 76RES4106

	Initial	After Hot Rolling At 400° F	
		24 Hours	72 Hours
E.S., volts[a]	736	367	307
Dial reading[b],			
600 rpm	96	106	85
300 "	62	63	49
200 "	50	50	37
100 "	34	33	24
6 "	21	11	7
3 "	20	10	6
Gel Strength[c], 10 sec/10 min	20/20	10/20	6/17
PV, cp[d]	34	43	36
YP, lbs/100sqft[e]	28	20	13
HTHP fluid loss, ml[f]	3	44	36
Top oil separation, ml[g]		23	25

TABLE XIII (continued)

D. 76RES4470

	Initial	After Hot Rolling At 400° F 24 Hours	72 Hours
E.S., volts[a]	917	318	277
Dial reading[b],			
600 rpm	99	102	106
300 "	62	58	58
200 "	49	42	43
100 "	33	27	25
6 "	20	6	5
3 "	19	5	4
Gel Strength[c], 10 sec/10 min	19/28	5/10	4/10
PV, cp[d]	37	44	48
YP, lbs/100sqft[e]	25	14	10
HTHP fluid loss, ml[f]	4	10	20
Top oil separation, ml[g]		13	21

a.-g. See Table V, footnotes.

The data listed in above Table XIII indicate that each of the four different styrene/butadiene polymers listed in Table I yields a drilling fluid having overall satisfactory characteristics for use at elevated temperatures when formulated in accordance with the present invention.

EXAMPLES 12-18

EFFECT OF VARYING SULFONATED ELASTOMER POLYMERIC VISCOSIFIER AND POLYMERIC FLUID LOSS CONTROL AGENT CONCENTRATIONS

Seven exemplary oil-base drilling fluids (about 5 lab barrels each) were formulated using varying sulfonated elastomer polymeric viscosifier and polymeric fluid loss control agent concentrations as shown in the following Table XIV:

TABLE XIV

Component	Quantity	Mixing Time, minutes
Mentor 26 brand oil	205 ml (0.586 bbl)	N/A[a]
Inventone 38H brand amine-treated hectorite	3 ppb	30[b]
Versamul I brand primary emulsifier	4 ppb	
Versacoat I brand oil wetting agent	5 ppb	10
Versawet I brand surfactant	3 ppb	
Lime ($Ca(OH)_2$)	10 ppb	10
Brine solution		30
Water	51.5 ml (0.147 bbl)	
$CaCl_2$	26.3 ppb	
Versatrol brand gilsonite	10 ppb	15
Barite	269 ppb	20
HT brand polymeric fluid loss control agent	varied	10
Tek Mud 1949 brand sulfonated elastomer polymeric viscosifier	varied	35

a. N/A denoted not applicable.

b. The amine-treated hectorite was slowly added to the oil.

One sample was used to check the initial rheological properties and either single or duplicate samples were used to check the rheological properties after being aged for about 72 hours. Each age-tested sample was placed into an aging bomb in the presence of about 100 psi nitrogen and rolled at about 400° F. After aging, the amount of top oil separation was measured and the consistency of the drilling fluid noted. The age-tested samples were then remixed and their rheological properties checked. Both the initial and age-tested rheological properties were measured at about 150° F. The results are noted below in Table XV.

TABLE XV

HT Polymer, ppb	0		3		6	
Tek Mud, ppb	1		1		1	
	Initial	Aged	Initial	Aged	Initial	Aged
E.S., volts[a]	850	310	814	263	620	322
Dial reading[b],						
600 rpm	94	77	106	105	110	95
300 "	60	42	66	59	70	56
200 "	48	30	52	43	56	42
100 "	33	19	36	27	38	28
6 "	19	4	22	7	21	7.5
3 "	18	3	21	6	20	6.5
Gel Strength[c], 10 sec/10 min	18/26	3/7	21/30	6/5	20/33	6/13
PV, cp[d]	34	35	40	46	40	39
YP, lbs/100sqft[e]	26	7	26	13	30	17
HTHP fluid loss, ml[f]	5	90	4	41	1.4	4
Top oil separation, ml[g]		27		29		18

TABLE XV (continued)

HT Polymer, ppb	9		12	
Tek Mud, ppb	1		1	
	Initial	Aged	Initial	Aged
E.S., volts[a]	834	350	710	372
Dial reading[b],				
600 rpm	134	114	162	114
300 "	88	69	105	69
200 "	71	54	84	56
100 "	51	36	66	37
6 "	31	13	48	15
3 "	30	11	45	13
Gel Strength[c], 10 sec/10 min	30/45	11/22	45/84	13/25
PV, cp[d]	46	45	57	45
YP, lbs/100sqft[e]	42	24	48	24
HTHP fluid loss, ml[f]	1.6	21	2	6
Top oil separation, ml[g]		19		0

TABLE XV (continued)

HT Polymer, ppb	6		6		6	
Tek Mud, ppb	0		0.5		1.5	
	Initial	Aged	Initial	Aged	Initial	Aged
E.S., volts[a]	677	232	882	299	734	373
Dial reading[b],						
600 rpm	60	61	87	81	150	148
300 "	39	30	55	44	92	92
200 "	30	20	47	32	72	72
100 "	24	11	32	18	51	49
6 "	12	11	18	3	29	20
3 "	9	1	17	2	27	17
Gel Strength[c], 10 sec/10 min	9/18	1/1	17/18	2/5	27/37	17/28
PV, cp[d]	21	31	32	37	58	56
YP, lbs/100sqft[e]	18	-1	23	8	34	37
HTHP fluid loss, ml[f]	2.4	6	1.6	4	1.4	73
Top oil separation, ml[g]		N/A[h]		34		19

TABLE XV (continued)

HT Polymer, ppb	6		6	
Tek Mud, ppb	2		3	
	Initial	Aged	Initial	Aged
E.S., volts[a]	923	433	718	692
Dial reading[b],				
600 rpm	279	275	750	900+
300 "	183	164	618	600
200 "	147	129	540	459
100 "	105	89	441	258
6 "	60	42	201	60
3 "	54	38	168	60
Gel Strength[c], 10 sec/10 min	54/84	38/50	165/225	48/96
PV, cp[d]	96	111	132	TV[i]
YP, lbs/100sqft[e]	87	51	486	TV[i]
HTHP fluid loss, ml[f]	1.6	6.7	2.4	10
Top oil separation, ml[g]		17		0

a.-g. See Table V, footnotes.

h. N/A denotes not available.

i. TV denotes too viscous to obtain.

The data in above Table XV indicate that, for the concentrations ranges tested, best results were obtained when the drilling fluid of the present invention contained a polymeric fluid loss control agent concentration of about 6 ppb and a sulfonated elastomer polymeric viscosifier concentration of about 0.5 to about 1 ppb. Field observations indicate that lower concentrations of the polymeric fluid loss control agent and sulfonated elastomer polymeric viscosifier can be employed to give very acceptable results. This

observation is believed to be due to the presence in the drilling fluid of fine particle size materials that originate in the subterranean formation but do not separate from drilling fluid when the drilling fluid is processed to remove drill cuttings.

Although the present invention has been described in detail with reference to some preferred versions, other versions are possible. Therefore, the spirit and scope of the appended claims should not necessarily be limited to the description of the preferred versions contained herein.

CLAIMS

1. An oil-base drilling fluid comprising oil, a surfactant, a fluid loss control agent, and a viscosifier, characterized in that the fluid loss control agent is selected from the group consisting of polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene, natural rubber, butyl rubber, polymers consisting of at least two monomers selected from the group consisting of styrene, butadiene, isoprene, and vinyl carboxylic acid, and mixtures thereof and the viscosifier is a sulfonated elastomer polymer.

2. The oil-base drilling fluid of claim 1 wherein the sulfonated elastomer polymer is a neutralized sulfonated elastomer polymer having about 5 to about 100 milliequivalents of sulfonate groups per 100 grams of sulfonated polymer.

3. The oil-base drilling fluid of claim 1 wherein the sulfonated elastomer polymer is derived from an elastomer polymer selected from the group consisting of ethylene-propylene-diene monomer (EPDM) terpolymers, copolymers of isoprene and styrene sulfonate salt, copolymers of chloroprene and styrene sulfonate salt, copolymers of isoprene and butadiene, copolymers of styrene and styrene sulfonate salt, copolymers of butadiene and styrene sulfonate salt, copolymers of butadiene and styrene, terpolymers of isoprene, styrene, and styrene sulfonate salt, terpolymers of butadiene, styrene, and styrene sulfonate salt, butyl rubber, partially hydrogenated polyisoprenes, partially hydrogenated polybutylene, partially hydrogenated natural rubber, partially hydrogenated buna rubber, partially hydrogenated polybutadienes, and Neoprene.

4. The oil-base drilling fluid of claim 1 wherein the fluid loss control agent is a styrene-butadiene copolymer.

5. The oil-base drilling fluid of claim 1 comprising about 3 to about 12 pounds per barrel (ppb) of the

fluid loss control agent and about 0.02 to about 2 ppb of the sulfonated elastomer polymer.

6. The oil-base drilling fluid of claim 1 comprising about 5 to about 10 pounds per barrel (ppb) of the fluid loss control agent and about 0.5 to about 1.5 ppb of the sulfonated elastomer polymer.

7. The oil-base drilling fluid of claim 6 comprising about 6 to about 9 ppb of the fluid loss control agent.

8. The oil-base drilling fluid of claim 1 wherein the weight ratio of (a) the fluid loss control agent to (b) the sulfonated elastomer polymer is about 1.5:1 to about 50:1.

9. The oil-base drilling fluid of claim 1 wherein the weight ratio of (a) the fluid loss control agent to (b) the sulfonated elastomer polymer is about 3:1 to about 20:1.

10. The oil-base drilling fluid of claim 1 wherein the weight ratio of (a) the fluid loss control agent to (b) the sulfonated elastomer polymer is about 5:1 to about 10:1.

11. The oil-base drilling fluid of claim 1 further comprising water.

12. The oil-base drilling fluid of claim 1 further comprising lime.

13. The oil-base drilling fluid of claim 1 further comprising a weighting agent.

14. The oil-base drilling fluid of claim 1 further comprising a shale inhibiting salt.

15. An oil-base drilling fluid weighing about 7.5 to about 20 pounds per gallon and comprising:

(a) about 25 to about 85 volume percent oil based on the total volume of the fluid;

(b) about 1 to about 20 pounds per barrel (ppb) surfactant;

(c) up to about 45 volume percent water based on the total volume of the fluid;

(d) up to about 600 ppb weighting agent;

(e) about 0.5 to about 30 ppb organophilic clay;

(f) up to about 30 ppb auxiliary fluid loss control agent;

(g) about 3 to about 12 ppb polymeric fluid loss control agent selected from the group consisting of polystyrene, polybutadiene, polyethylene, polypropylene, polybutylene, polyisoprene, natural rubber, butyl rubber, polymers consisting of at least two monomers selected from the group consisting of styrene, butadiene, isoprene, and vinyl carboxylic acid, and mixtures thereof;

(h) about 0.02 to about 2 weight percent sulfonated elastomer polymeric viscosifier;

(i) up to about 60 ppb shale inhibiting salt; and

(j) up to about 30 ppb lime.

16. The oil-base drilling fluid of claim 15 weighing about 9 to about 16 pounds per gallon and comprising:

(a) about 50 to about 60 volume percent oil based on the total volume of the fluid;

(b) about 1 to about 10 ppb surfactant;

(c) about 10 to about 20 volume percent water based on the total volume of the fluid;

(d) about 150 to about 400 ppb weighting agent;

(e) about 1 to about 10 ppb organophilic clay;

(f) about 2 to about 15 ppb auxiliary fluid control agent;

(g) about 5 to about 10 ppb polymeric fluid control agent;

(h) about 0.5 to about 1.5 weight percent sulfonated elastomer polymeric viscosifier;

(i) about 20 to about 30 ppb shale inhibiting salt; and

(j) about 1 to about 10 ppb lime.

17. The oil-base drilling fluid of claim 15 wherein the auxiliary fluid control loss agent is selected form the group consisting of amine-treated lignite, gilsonite, asphaltics, and mixtures thereof.

18. A drilling system comprising:

(a) at least one subterranean formation;

(b) a borehole penetrating a portion of at least one of the subterranean formations;

(c) a drill bit suspended in the borehole; and

(d) a drilling fluid located in the borehole and proximate the drill bit,

wherein the drilling fluid is the oil-base drilling fluid of claim 1.

19. A drilling system comprising:

(a) at least one subterranean formation;

(b) a borehole penetrating a portion of at least one of the subterranean formations;

(c) a drill bit suspended in the borehole; and

(d) a drilling fluid located in the borehole and proximate the drill bit,

wherein the drilling fluid is the oil-base drilling fluid of claim 15.

20. A method for drilling a borehole in a subterranean formation, the method comprising the steps of:

(a) rotating a drill bit at the bottom of the borehole and

(b) introducing a drilling fluid into the borehole (i) to pick up drill cuttings and (ii) to carry at least a portion of the drilling cuttings out of the borehole, wherein the drilling fluid is the oil-base drilling fluid of claim 1.

21. A method for drilling a borehole in a subterranean formation, the method comprising the steps of:

(a) rotating a drill bit at the bottom of the borehole and

(b) introducing a drilling fluid into the borehole (i) to pick up drill cuttings and (ii) to carry at least a portion of the drilling cuttings out of the borehole, wherein the drilling fluid is the oil-base drilling fluid of claim 15.

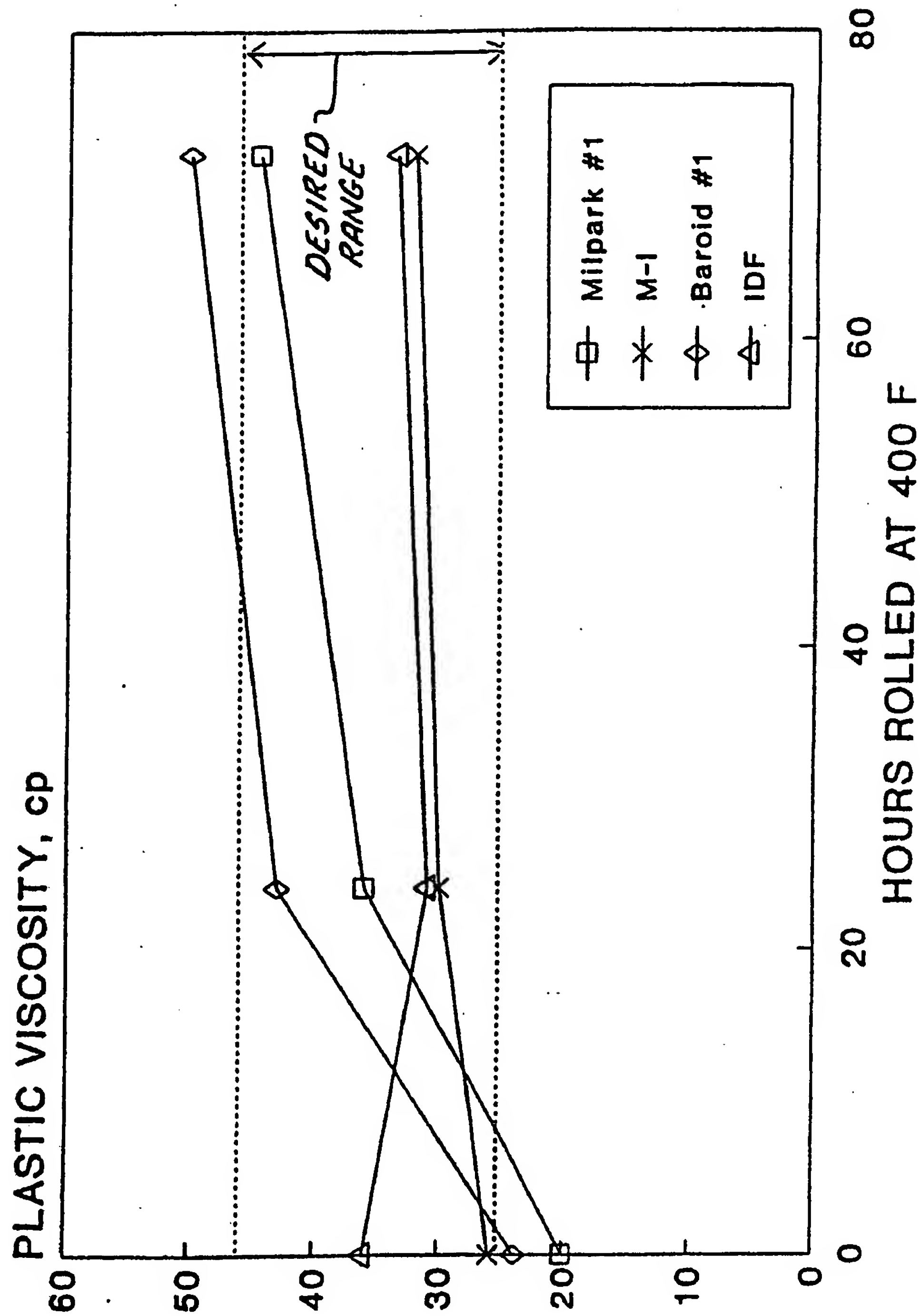
PLASTIC VISCOSITY, cp
HOURS ROLLED AT 400 F
DESIRED RANGE
Milpark #1
M-I
Baroid #1
IDF
0
10
20
30
40
50
60
0
20
40
60
80

FIGURE 1

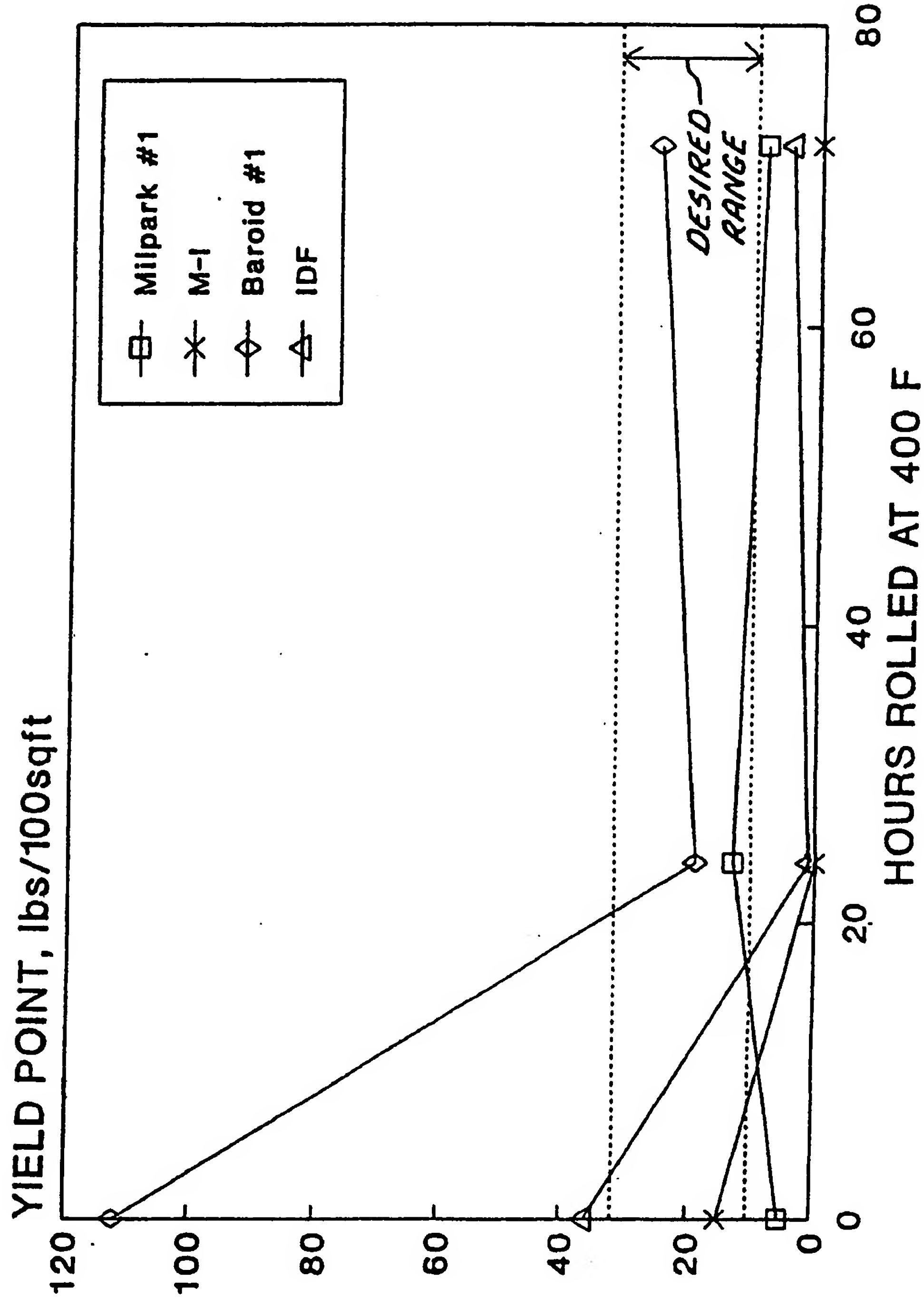
YIELD POINT, lbs/100sqft
120
100
80
60
40
20
0
Milpark #1
M-I
Baroid #1
IDF
DESIRED RANGE
0
20
40
60
80
HOURS ROLLED AT 400 F

FIGURE 2

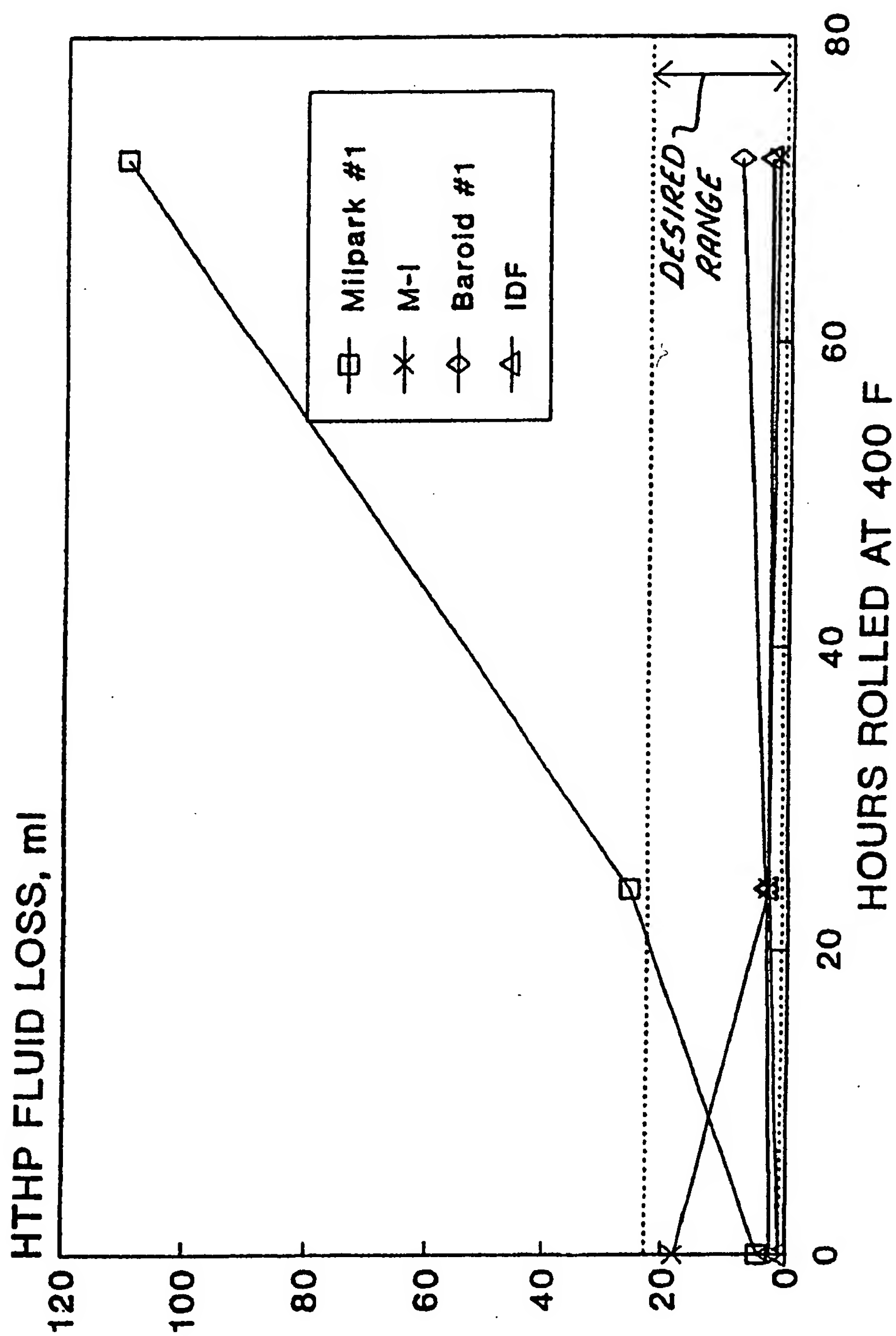
HTHP FLUID LOSS, ml
120
100
80
60
40
20
0
0
20
40
60
80
HOURS ROLLED AT 400 F
Milpark #1
M-I
Baroid #1
IDF
DESIRED RANGE

FIGURE 3

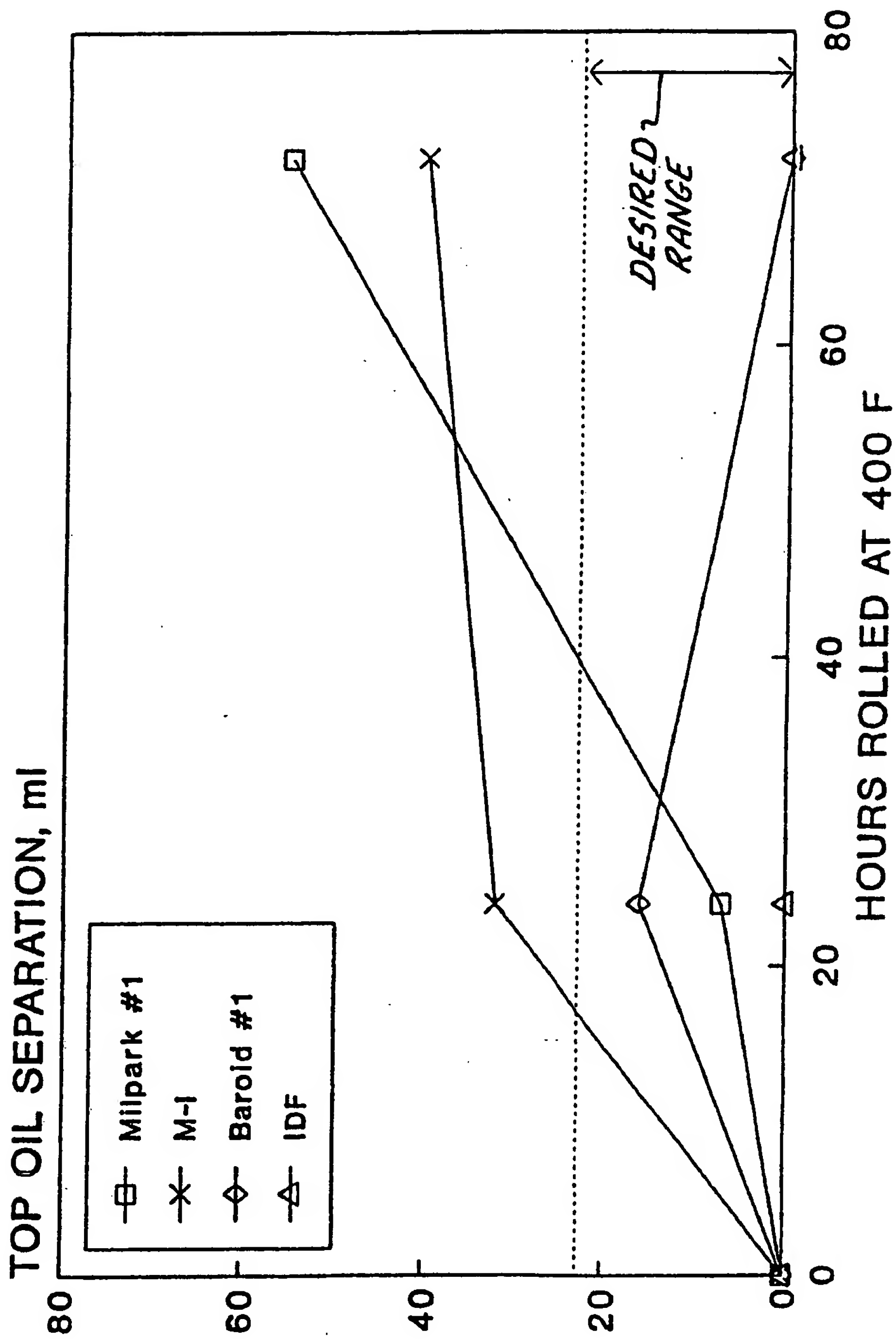
TOP OIL SEPARATION, ml
80
60
40
20
0
0
20
40
60
80
HOURS ROLLED AT 400 F
Milpark #1
M-I
Barold #1
IDF
DESIRED RANGE

FIGURE 4

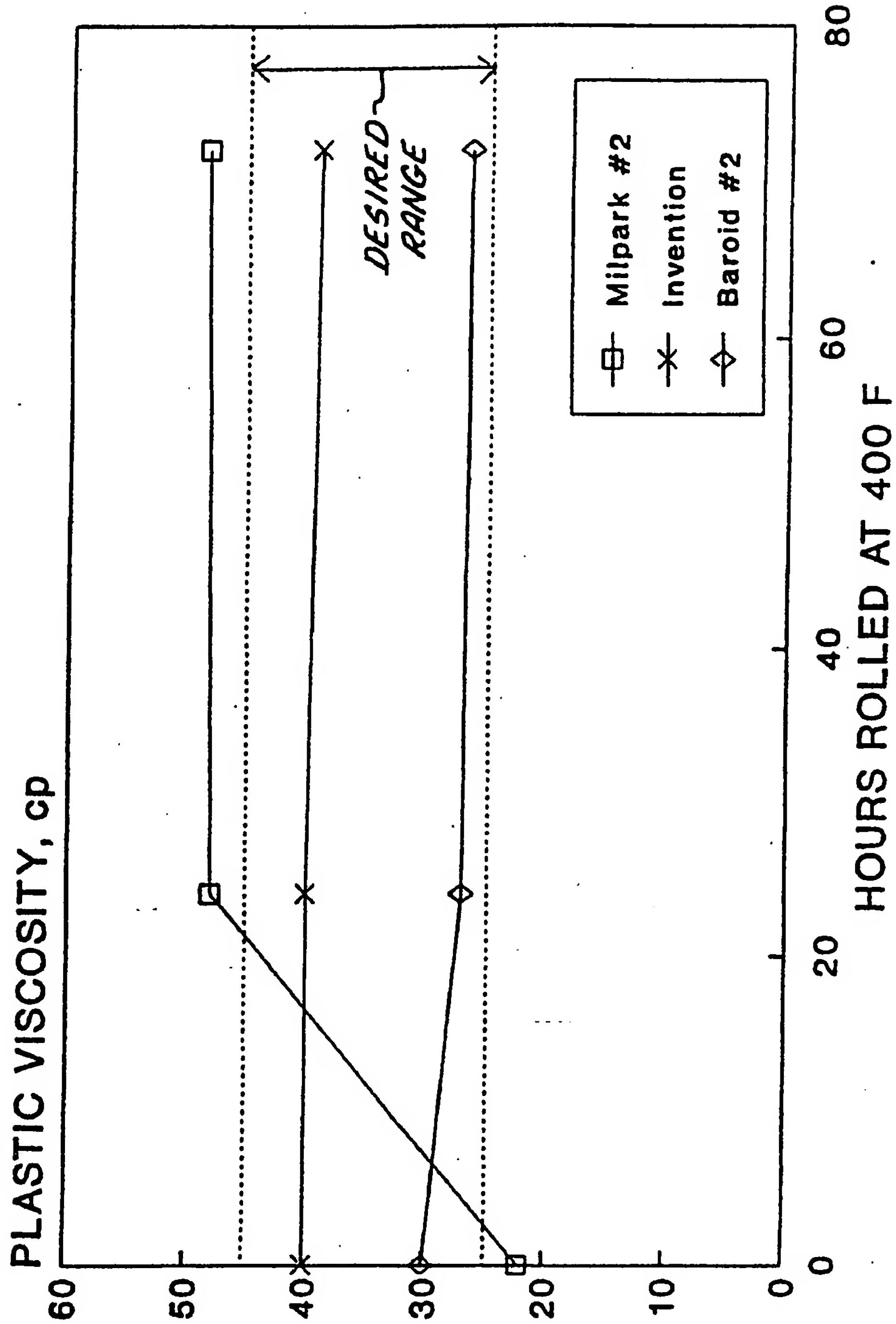
PLASTIC VISCOSITY, cp
60
50
40
30
20
10
0
0
20
40
60
80
HOURS ROLLED AT 400 F
DESIRED RANGE
Milpark #2
Invention
Baroid #2

FIGURE 5

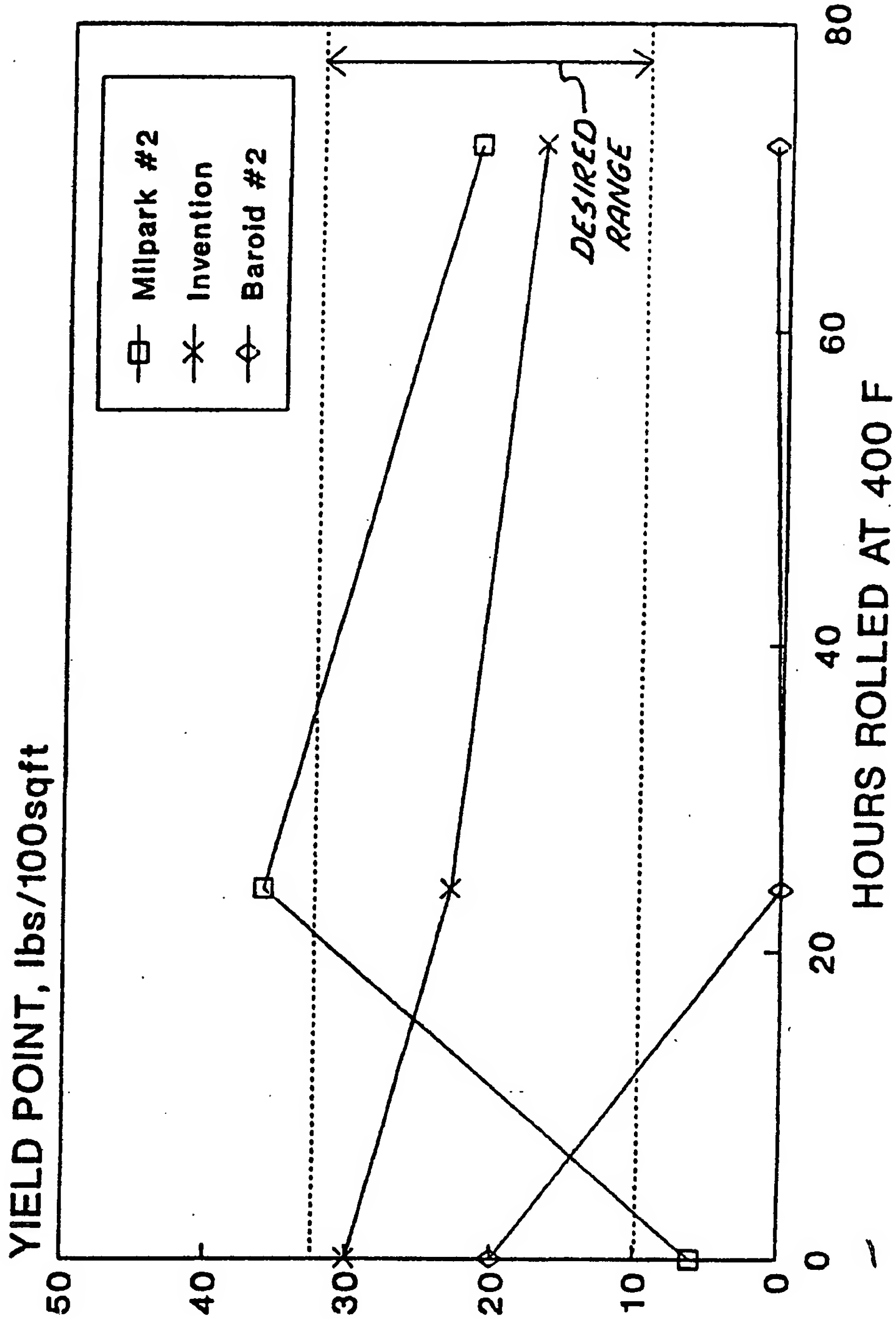
YIELD POINT, lbs/100sqft
50
40
30
20
10
0
0
20
40
60
80
HOURS ROLLED AT 400 F
Milpark #2
Invention
Baroid #2
DESIRED RANGE

FIGURE 6

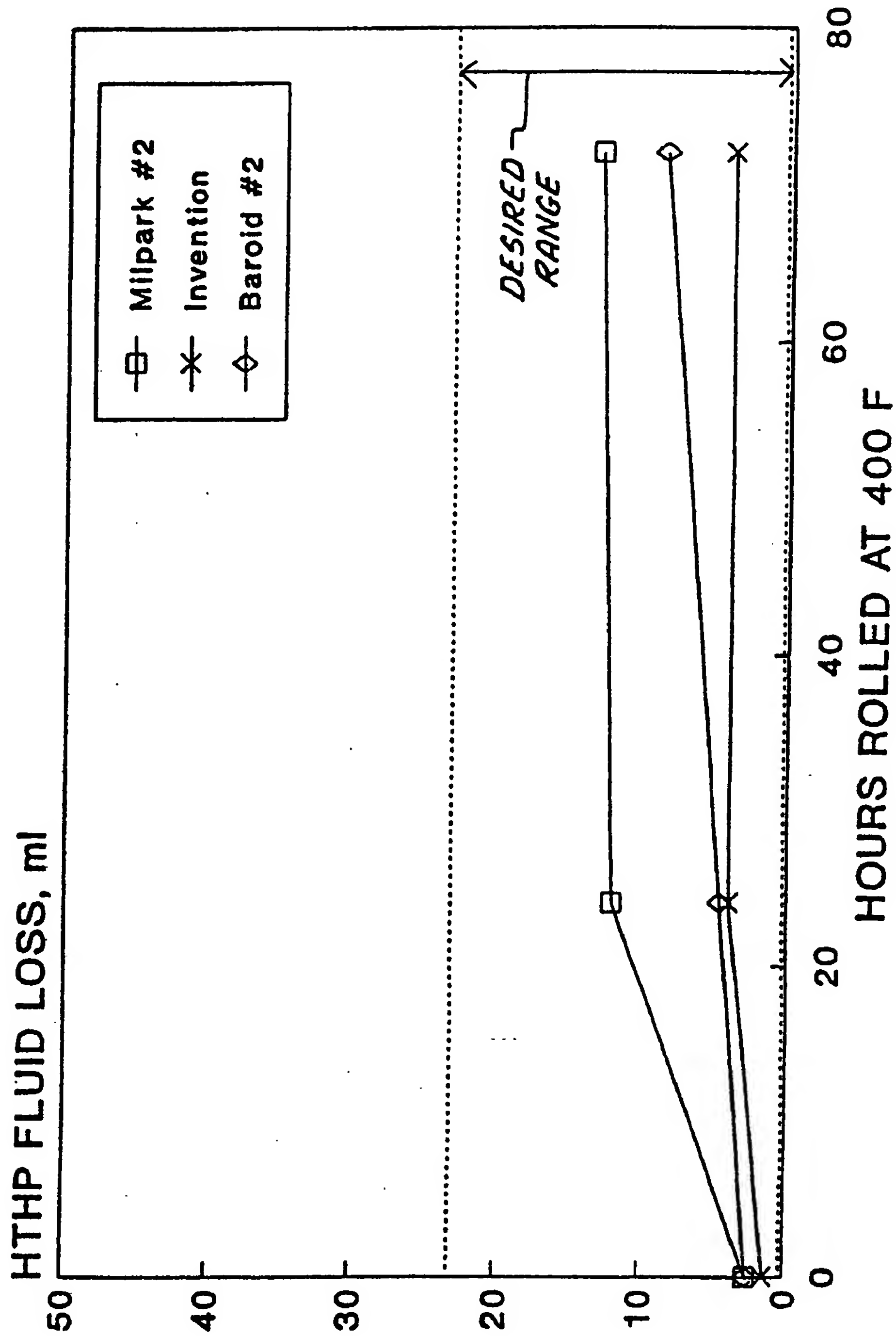
HTHP FLUID LOSS, ml
50
40
30
20
10
0
Milpark #2
Invention
Baroid #2
DESIRED RANGE
0
20
40
60
80
HOURS ROLLED AT 400 F

FIGURE 7

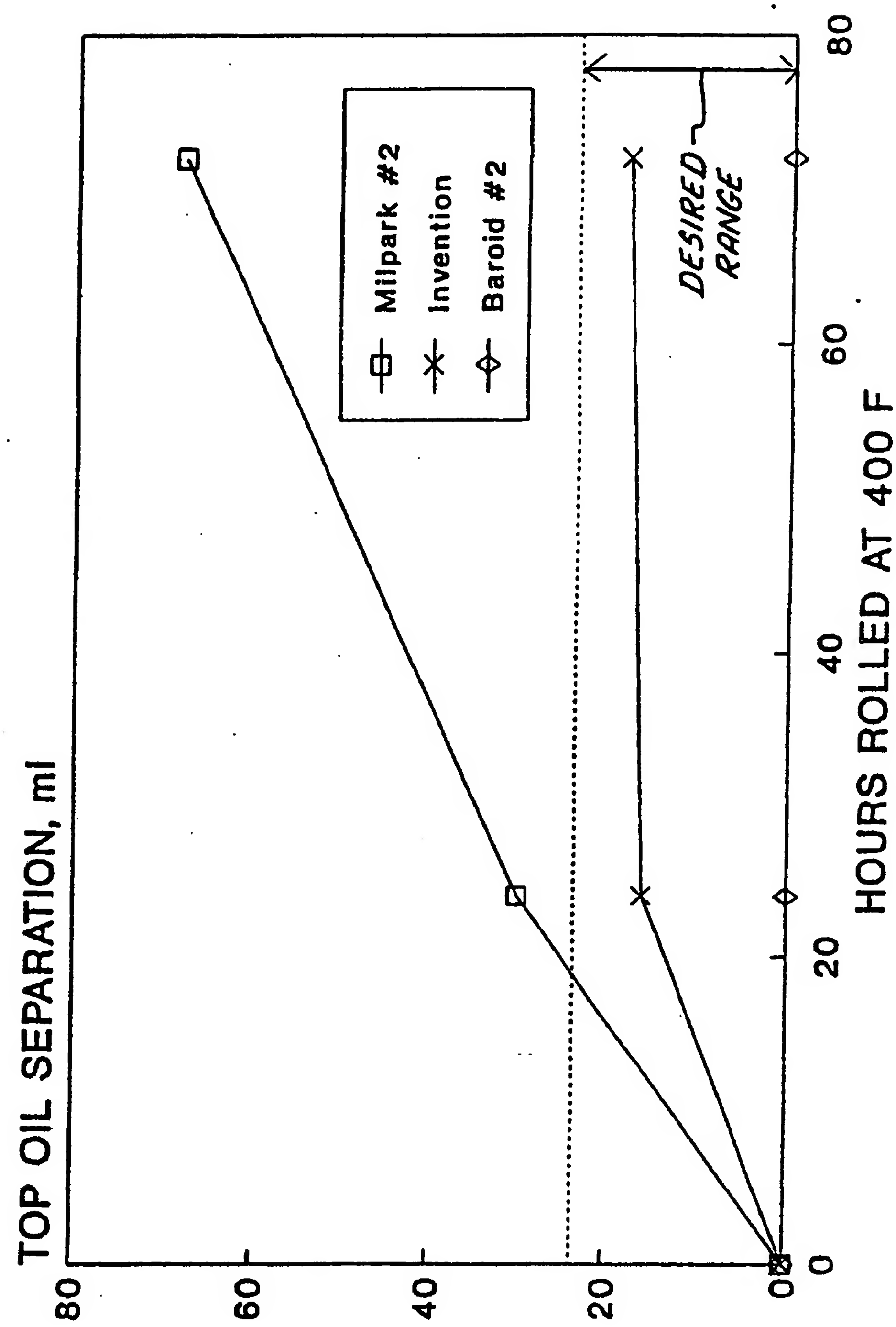
TOP OIL SEPARATION, ml
80
60
40
20
0
0
20
40
60
80
HOURS ROLLED AT 400 F
Milpark #2
Invention
Baroid #2
DESIRED RANGE

FIGURE 8

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/09160

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C09K7/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C09K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
Y	US,A,4 537 919 (P.K.AGARWAL) 27 August 1985 see column 1, line 38 - column 2, line 19 see column 4, line 49 - column 5, line 29	1,3,4, 15-17
Y	US,A,3 351 079 (D.L.GIBSON) 7 November 1967 see column 1, line 47 - line 60 see column 2, line 6 - column 3, line 42	1,4, 15-17
Y	US,A,4 537 688 (D.G.PEIFFER) 27 August 1985 see column 2, line 27 - column 3, line 21	1,3, 15-17
Y	US,A,4 442 011 (W.A.THALLER) 10 April 1984 see column 2, line 46 - column 3, line 37	1,3, 15-17

[o] Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
22 JANUARY 1993	28. 01. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BOULON A.F.J.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9209160
SA 66423

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 22/01/93
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4537919	27-08-85	None	
US-A-3351079		None	
US-A-4537688	27-08-85	None	
US-A-4442011	10-04-84	None	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82